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# EFFECT OF PARTIALLY REACTING $Nb_3Sn$ BEFORE MAGNET WINDING ON THE STRAND CRITICAL CURRENT

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## ABSTRACT

$Nb_3Sn$ is currently the material most commonly foreseen for the development of high field superconducting magnets. This is done by either the wind and react technique, usually used for compact magnets like accelerator magnets, or the react and wind technique, more common on large scale magnets. In both cases, a thorough understanding of the Cu-Sn system diffusion and phase formation processes is necessary to optimize the $Nb_3Sn$ reaction cycle. Attention has to be paid to both the superconducting performance and the prevention of thermally induced damage of the final produced conductor. The formation of the eta and epsilon phases of the Cu-Sn phase diagram were investigated as a function of time and temperature. Wherever possible, the activation energies and diffusion coefficients were calculated. The feasibility of winding partly reacted cables to reduce the manufacturing time was also explored. $Nb_3Sn$ strands have been partially reacted to convert the Sn to the eta and epsilon phases of the Cu-Sn phase diagram, then plastically strained to figure out a cabling and/or a winding degradation. After completion of the reaction cycle, the critical current was measured and compared with that obtained with an uninterrupted cycle.

## INTRODUCTION

The reaction cycle required to produce the superconducting $Nb_3Sn$ phase by a diffusion process of the Tin trough the Copper matrix is a critical step in the manufacturing process of a magnet. The final properties of the superconducting material are gained during this operation and risk of wire burst or local inhomogeneity due to overpressure may happen. The cost of this time consuming operation involving expensive tooling is also important. By improving the understanding of the copper tin diffusion process, we have tried to reduce the risk and the cost of the heat treatment. Superconducting strands have been prereacted to form the first intermetallic compounds of the Copper Tin diagram, thus suppressing the risk associated with the liquid phase of Tin, then mechanical strain has been applied to figure out the winding process. After completion of a full reaction cycle at 700C, the critical current has been measured and compared to reference values from the same strands.

## DIFFUSION MODELS

Intermetallic diffusion has been widely studied, especially in relation with welding operations[(1)]. The equation relating the thickness of an intermetallic layer y with time t is:

$$Y^n = k(T)\ (t - t_0)$$

Where k is the diffusion coefficient and depends on temperature, n has a value around 2, and $t_0$ is the lag time or time required to form a continuous intermetallic layer at the interface. Plotting Ln(y) as a function of

Ln($t - t_0$) gives a straight line having a slope of value 1/n, and allows the determination of k. Expressing the diffusion coefficient k as a function of temperature T allows to access the activation energy E of the diffusion process, the slope of the plot of –Ln(k) as a function of 1/T being equal to E/R, where R is the Boltzmann constant. This approach is appropriate to solid/solid diffusion. The mean value of the thickness y can be calculated from the measurement of the surface area over a length of the interface using image analysis.

## DIFFUSION EXPERIMENTS

### Sample preparation

Diffusion samples were prepared by casting liquid Tin (Sn) in Copper (Cu) containers. Copper and Tin have been supplied by Intermagnetic General Corporation (IGC) and are of the same quality than those used for superconductor manufacturing. Initially a bore of 11 mm in diameter was machined axially in copper bars and filled with tin. After each heat treatment sequence a transverse slice of Copper and Tin was removed using a slow rotary saw, and then polished. After the observation that the eta phase growing in the liquid tin could separate from the interface and either fall in the liquid Tin or float in it, the samples were modified. The copper bars were drilled transversally with several holes 5 mm in diameter, and 15 mm in depth, and filled with Tin. After each heat treatment sequence a transverse slice that included a tin filled hole was removed, and cut in two halves in the middle of the hole. Heat treatments were conducted in a small furnace, with the diffusion samples sealed in pyrex tubes with a nitrogen coverage. The samples in their sealed tubes were introduced in a preheated furnace. At the end of the treatment they were removed from the furnace and allowed to cool down at room temperature. Since the Tin was in liquid form in most of the samples, quenching the samples in cold water was not feasible.

### Observations of the diffusion samples

Figure 1 shows the intermetallic growth on two samples. Figure 1-a shows a case of intermetallic diffusion at a solid/solid interface, while Figure 1-b shows a solid/liquid interface. In both pictures the two intermetallic compounds eta and epsilon are present. Except in the case of the growth of the eta phase inside liquid tin, the thickness of the intermetallic layer is almost uniform along the interface. When the eta intermetallic develops inside the liquid, it forms large crystals as seen on figure 1-b. It should be noted on figure 1-b that voids have been created inside the epsilon phase. This effect comes from the difference of density between the two intermetallic compounds, the epsilon phase having the higher density.

A sample has also been cut and observed just after the casting of the Tin in the Copper to see if intermetallics were still present. Some spots of eta phase were observed.

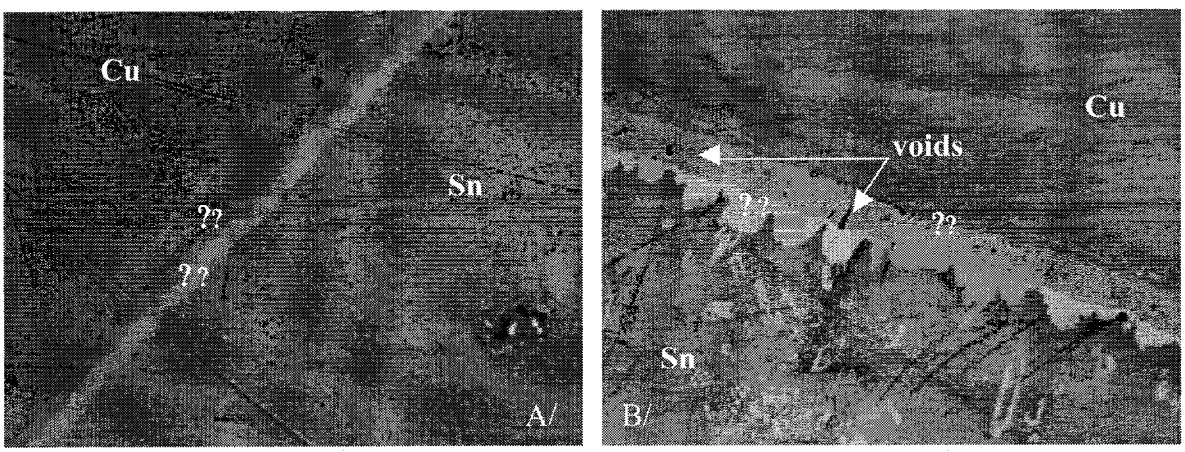



**FIGURE 1:** Intermetallic growth at the Cu/Sn interface **a/** after 7 days at 210C, **b/** after 2 days at 400C.

### Diffusion measurements

Thickness measurements have been performed using a Nikon optical microscope and a Spot software. The surface area of the intermetallic layers have been measured and divided by the length of the interface to determine the mean thickness of the layer. The measurement has been repeated in 4 location for each sample. This allows an estimation of the mean thickness over a length of 50 ?m, the precision of the measurement being better than 10% in the case of solid/solid diffusion. Figure 2 shows the plots of the thickness evolution of each phase as a function of time for the different temperatures.

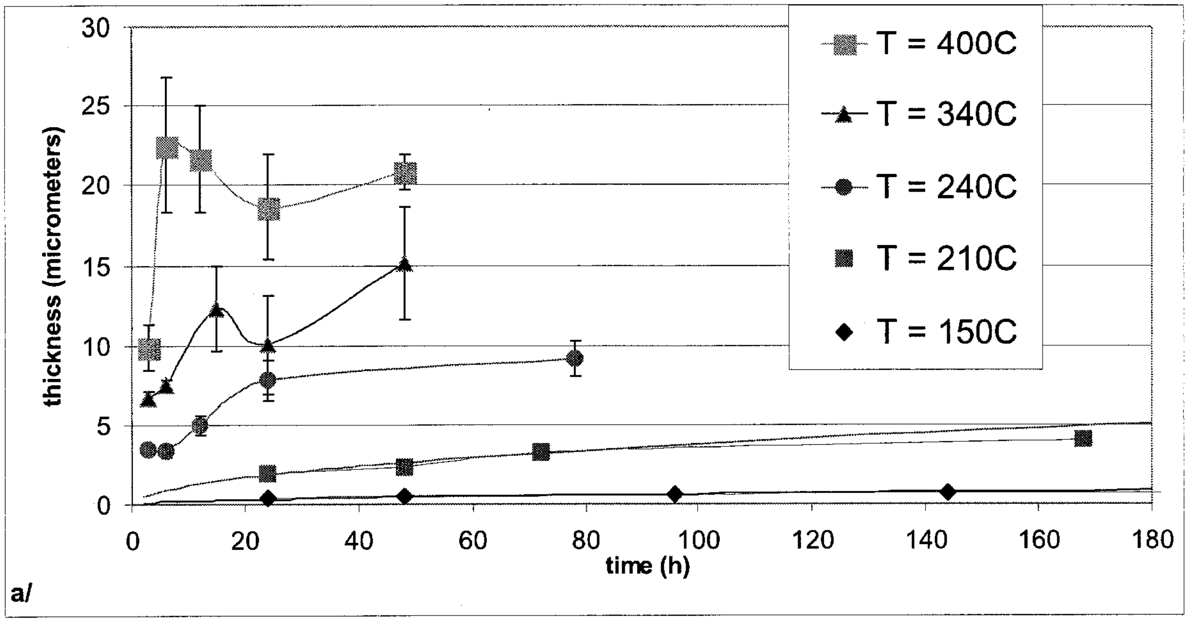



**FIGURE 2: a** / thickness of the eta phase as a function of time and temperature.

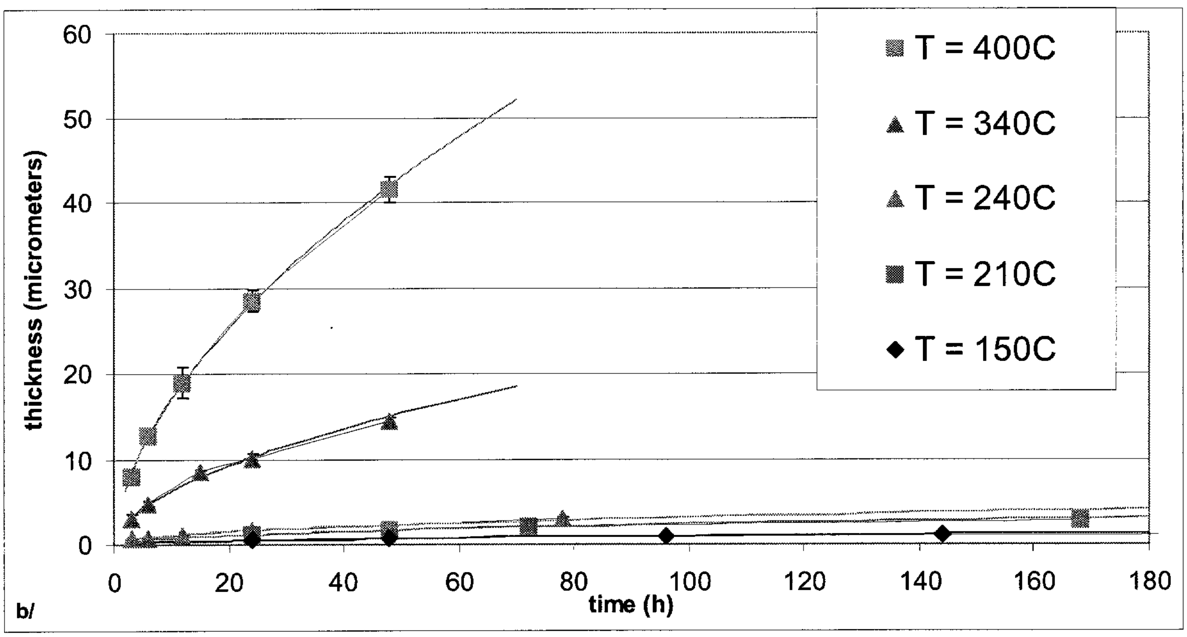



**FIGURE 2: b** / thickness of the epsilon phase as a function of time and temperature. Experimental points and growth curves plotted using the values presented in table 1.

Once the Sn becomes liquid (i.e. at 240C, 340C and 400C), the mean thickness of the eta phase shown in figure 2-a can not be interpreted using a solid/solid diffusion model. The large error bars reflect the scatter in the grain size that are growing in the liquid Tin. From figure 2 it is clear that the diffusion of Sn in Copper is more effective as soon as Tin becomes liquid. The rates of growth of the eta and epsilon phases are low at 150C and 210C, and are both of the same order of magnitude. The growth of the eta phase shows a significant increase above 210C. In the same temperature range the diffusion of the epsilon phase increases and is strongly temperature dependent between 240C and 400C.

Table 1 gives the thickness exponent and the diffusion coefficient of the eta, epsilon and delta phases. Considering the very low rate of growth of the eta and epsilon phases at 150C and 210C, the thickness exponent has been fixed equal to 2 to determine the diffusion coefficient. This assumption is realistic when the growth rate is slow[1], the diffusion of each species and the concentration gradient being almost constant. The value of $t_0$ used for the diffusion analysis has been considered equal to 0.25 h for each phase.

**TABLE 1.** Thickness exponent and diffusion coefficient (in $m^2/s$) for the different phases.

| Temperature | Eta phase | Eps phase | Delta phase |
| --- | --- | --- | --- |
| 150 C | N = 2<br>K = 1.2 $10^{-18}$ | N = 2<br>K = 3 $10^{-18}$ | |
| 210 C | N = 2<br>K = 4 $10^{-17}$ | N = 2<br>K = 1.6 $10^{-17}$ | |
| 240 C | | N = 2.24<br>K = 1.4 $10^{-18}$ | |
| 340 C | | N = 1.83<br>K = 9.1 $10^{-15}$ | |
| 400 C | | N = 1.75<br>K = 1.25 $10^{-13}$ | |
| 440 C | | | N = 1.37<br>K = 7.2 $10^{-10}$ |

Using the values of diffusion coefficient presented in table 1 the activation energy for the growth of the epsilon phase between 240C and 400C has been determined to be 5.1 kJ/mole.

The value of the activation energy below the melting point of Tin is lower than the one found in bibliography[2] for similar intermetallic compounds. The growth rate of the epsilon phase once the Tin is molten is much lower than when the Tin is solid.

## CRITICAL CURRENT MEASUREMENTS

### Reaction cycle

Two different strands have been used for the critical current measurements. The ITER strand has been made using an Internal Tin (IT) process, while the OST strand is manufactured with the Modified Jelly Roll (MJR) technique. Their characteristics are presented in table 2. Extensive studies on these strands provide a good benchmark of their characteristics[3,4].

The reaction cycle have been conducted in two successive steps, with a mechanical solicitation between the two steps. The first part of the reaction cycle has been conducted in order to react the Tin prior of the Nb3Sn formation. It has been realized in a sealed pyrex tube with a Nitrogen coverage. In one case we have prereacted the strands at 210C for one week, expecting the Tin to diffuse completely in the Copper in a pure solid/solid diffusion process; in the other the pre-reaction cycle has been made at 400C for 48 hours, in a liquid/solid diffusion process. Detailed reaction cycles are presented in table 3. At the end of the pre-reaction cycle, the pyrex tubes were opened, and the wire wound on the titanium supports used for the final heat treatment and the critical current measurement.

**TABLE 2.** Strand Specifications.

| Parameter | ITER Strand[4] | OST Strand[3] |
| --- | --- | --- |
| Strand diameter, mm | 1 ? 0.005 | 1.001 ? 0.001 |
| $J_c$(12 T, 4.2 K), A/mm$^2$ | > 700 | > 1950 |
| $I_c$(12 T, 4.2 K), A | > 200 | > 800 |
| $d_{eff}$, ?m | < 3-5 | < 110 |
| Cu, % | 58.7 ? 0.3 | > 48 ? 0.3 |
| RRR | > 200 | < 20 |
| Twist pitch, mm/turn | 25 ? 10 | 13 ? 3 |

**TABLE 3.** Heat Treatment Cycles.

| Heat Treatment | | 1 | 2 |
|---|---|---|---|
| **Pre-reaction** | Ramp rate, °C/h | 25 | 400 |
| | Temperature, °C | 210 | 400 |
| | Duration, h | 168 | 48 |
| **Nb3Sn formation** | Ramp rate, °C/h | 30 | 30 |
| | Temperature, °C | 400 | 400 |
| | Ramp rate, °C/h | 6 | 6 |
| | Temperature, °C | 700 | 700 |
| | Duration, h | 40 | 40 |

**Observation of the pre-treated strands**

Short lengths of the pre-reacted strands were kept for microscopic observations. Figure 3 shows the sections of the ITER strand at the end of the preliminary treatment. After 7 days at 210C (figure 3-a) a substantial part of the Tin is still unreacted. It should be noted that the layer of the intermetallic compounds appearing around the Tin pools between the subelements is thicker than the same layer growing inside the subelements. After 2 days at 400C (figure 3-a) the Tin has been completely converted into epsilon phase. Some voids have been formed during the reaction in the epsilon phase, as observed in the diffusion samples.

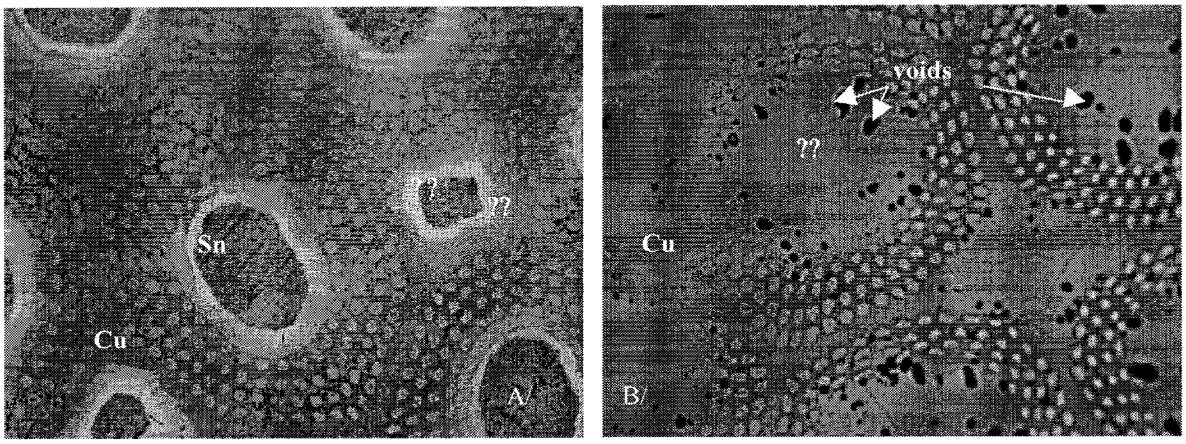



**FIGURE 3:** Intermetallic growth in the ITER strands: **a/** after 7 days at 210C, **b/** after 2 days at 400C.

**Sample Preparation and critical current measurement**

The samples used for Ic measurements were wound on grooved cylindrical Ti-alloy (Ti-6Al-4V) barrels, and held in place by two removable end rings[(5)]. After the heat treatment, the Ti-alloy end rings were replaced by Cu rings, and voltage-current (VI) characteristics were measured in boiling He at 4.2 K, in a transverse magnetic field from 6T to 15T. The voltage was measured along the sample by means of voltage taps placed 50 cm apart. The Ic was determined from the VI curve using the $10^{-14}$ ? ?m resistivity criterion. The relative directions of external magnetic field and transport current were such as to generate an inward Lorentz force. Due to the latter and to the differential thermal contraction between sample and barrel, the specimen is subject to a tensile strain of up to 0.05 % at 12 T and 4.2 K. This leads to a systematic error in the 3 to 5% range on Ic. The n-values were determined in the $V(I_c)$ to $10?V(I_c)$ range by fitting the VI curve with the power law $V \sim I^n$. The estimated uncertainty of the $I_c$ measurements is within ?1% at 4.2K and 12T.

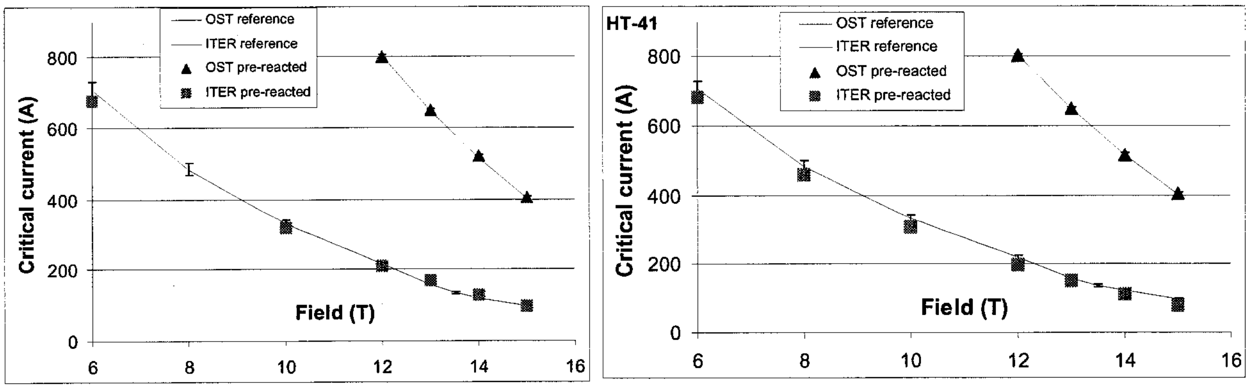
It is worthwhile to mention that the winding of the strands was not difficult and that the strands were not brittle as completely reacted $Nb_3Sn$ strands are. The strands had less spring back than before the pre-treatment, especially the one treated at 400C. This is due to the recristallization of the Copper on one hand, and to the fact that the volumic fraction of brittle intermetallic compounds is low on another.

The result of the critical current measurement are presented in figure 4, and compared to reference values measured on the same strands. The reference values are mean values of 7 measurements in the case of the ITER strand and of 5 measurements in the case of the OST strand. The measurements used to determine the reference values all use strands heat-treated at 700C during the final step. No degradation due to the pre-treatment to convert the Tin in the Eta and Epsilon intermetallic phases can be seen in figure 4.

The RRR (Residual Resistivity Ratio) of the strands has also been measured at the end of the heat treatment. Results are presented in table 4. The difference in RRR as a consequence of the pretreatment is attributed to the difference in technologies used to manufacture the strands.

**TABLE 4.** RRR measurements after the heat treatment cycles.

| | ITER Strand | OST Strand |
|---|---|---|
| Reference | 184 ? 40 | 23 ? 1 |
| Pre-treatment 210C - 7 days | 257 ? 34 | 17 |
| Pre-treatment 400C - 2 days | 203 | 37 ? 3 |




**a/** **b/**

**FIGURE 4:** Critical current of the pre-reacted ITER and OST strands compared to reference values for each strands. Pre-reaction cycle: **a/** 7 days at 210C, **b/** 2 days at 400C.

## CONCLUSION

We have shown that preliminary heat treatments on $Nb_3Sn$ superconducting wires can be made to convert the Tin in the intermetallic phases eta and epsilon prior to winding without generating degradation in the final superconducting properties of the strands. It is therefore possible to reduce substancially the time needed for the coil reaction, and the risk associated to this operation, by pre-reacting the cables before winding. This pre-reaction is efficient if the temperature of the strands is sufficient to melt the Tin, the growth rate of the epsilon phases being strongly temperature dependent. The formation of voids inside the strands can be related to successive phase transition during the Copper Tin interdiffusion process.


## ACKNOWLEDGMENT

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